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We review the transition melting studies carried out at Mainz, and describe a recently developed model used to explain that the relatively low melting slopes are due to the partially filled *d*-bands, and the persistence of the pressure induced *s*-*d* transition. The basic tenets of the model have now been reconfirmed by new measurements for Cu and Ni. The measurements show that Cu which has a filled 3*d*-band, has a melt slope that is about 2.5 greater than its neighbor Ni. In the case of Mo, the apparent discrepancy of DAC melting measurements with shock melting can be explained by accounting for the change in melt slope due to the bcc-cp transition observed in the shock studies. The Fe melt curve is revisited. The possible relevance of the Jahn-Teller effect and recently observed transition metal melts with Icosahedral Short-Range Order (ISRO) is discussed.

I. Introduction

Measurements of transition metal melting at extreme conditions employing laser-heated diamond-anvil cells (DAC) [1-4] have led to new theoretical insights into the systematics of melting according to crystal packing and electronic structure [5]. Fig. 1 shows some of the melting curves measured by the Mainz group. Note that the melting curves of Ar, Al and Cu differ significantly from the transition metals. Measurements for Ta made at the Advanced Photon Source (APS)[3], using x-ray diffraction to detect melting, have confirmed the low melting slopes (dT/dP) reported by the Mainz group.

In terms of the melting slopes, Ar, Al and Cu have the stiffest curves, the bcc metals Mo, Ta and W have unusually flat curves, while the fcc metals Fe, Co

and Ni are intermediate. Al is a nearly free electron polyvalent metal. Cu, unlike other transition metals, has a filled *d*-band below the Fermi surface that behaves as a repulsive core. In the case of metals with unfilled *d*-bands an important factor determining the melt slope is the s-d transition, which can only occur in a partially filled band. With increasing pressure *d*-electron density increases, and since the density of states will generally differ in the two phases, its effects will be evident in the melting slope (dT/dP). To test this view we recently examined the melting curves of Cu and Ni[4]. We found that the melt slope of Cu is about 2.5 greater than its neighbor Ni, which has an incompletely filled 3*d*-band.

In order to understand transition metal melting in a more quantitative sense we developed a semi-empirical model intended to encapsulate some of the above discussion, as well as evidence from recent experimental[6-8} and theoretical studies[9-11] which verify that melting in open shell transition metals leads to changes in the electronic structure. This paper is organized as follows. A brief description of the model is provided in Section II, and applied to Mo in Section III, where we propose a new phase diagram to reconcile an apparent discrepancy with shock melting. In the light of our new results, in Section IV we revisit Fe melting. In Section V we discuss the evidence for Icosahedral Short-Range Order (ISRO) structure in the melt and its relevance to melting . Section VI is a summary.

II. Model

Following suggestions by Ducastelle[12] and Pettifor[13] we write the total binding energy of a transition metal in the form, $U = U_{rep} + U_{d\text{-}band}$. U_{rep} is the repulsive contribution of the ions and *sp*-electrons, and $U_{d\text{-}band}$ is the cohesive energy of the *d*-band. U_{rep} is modeled by the inverse power potential (r^{-6}) equation of state determined from computer simulations[14]. The Friedel equation[15], $U_{d\text{-}band} = -\frac{W}{20} n_d (10 - n_d)$ is used to approximate the *d*-band density of states and cohesive energy. *W* is the bandwidth and n_d is the effective number of *d*-electrons/ion. In order to apply the theory model parameters, where available, need to be taken from the literature or approximated. While there is

some amount of information available for the solid there is little available for the liquid.

The Helmholtz free energy of the solid and liquid, is expressed in terms of the inverse power model[14],

$$F_e^s = U_{BM} + F_{th\_inv6}^s + U_{d\_band}^s \,, \qquad (1)$$

and

$$F_e^l = U_{BM} + F_{th\_inv6}^l + U_{d\_band}^l . \qquad (2)$$

U_{BM} is the lattice energy obtained here from Birch-Murgnahan (BM) fits to DAC room temperature isotherms adjusted to 0 K. The difference in free energy between the phases becomes,

$$\Delta F = (F_{th\_inv6}^l - F_{th\_inv6}^s) + \Delta U_{d\_band}^{l-s}, \qquad (3)$$

where $\Delta U_{d\_band}^{l-s} = (U_{d\_band}^l - U_{d\_band}^s)$. The term, in parenthesis, represents the change in the ion thermal free energy. The second term represents the change in *d*-band cohesive energy. This term has a negative value as a consequence of band broadening in the liquid or other changes like electron localization that may lower the liquid energy. The melting temperature is determined at a given volume for $\Delta F=0$. At constant volume the solid and liquid U_{BM} terms cancel. Since the volume change of melting for transition metals at high pressure are ~1%, the error introduced by equating Helmholtz free energies is small.

The formulation employed here bears some semblance to the Embedded-atom model in which the d-band cohesive energy is modeled as a glue-like embedded function[16]. Wills and Harrison[17] formulated an effective model potential for transition metals which, in spirit, is also similar to ours. It consists of two-body exponential and inverse power repulsive terms, and an attractive Friedel bonding term that differs from ours by varying as r^{-5}. As in our model, the W-H approach provides the possibility of treating the electronic properties of the solid and liquid differently. Our model is the simpler, but more easily suited for calculating phase equilibria.

III. Molybdenum phase diagram

Mo was originally studied because it has the flattest melting slope (dT/dP~0) of the transition metals studied and thereby provides the most severe test of the model. It was determined that a small broadening of the liquid *d*-band leads to a lowering of the liquid energy ΔU^{l-s}_{d-band}, by about ~1%, that is sufficient to depress the melting temperature to a value in agreement with diamond-anvil cell measurements[5]. These results are shown in Fig. 2. However, an extrapolation of the data well beyond 90 GPa appears to be in conflict with the results of sound speed measurements in shock compressed Mo[17,18]. An interpretation of the sound speed data in those experiments lead to the conclusion that breaks in the sound-speed data inferred a bcc-solid transition at 210 GPa and a melting point near 370 GPa.

To account for the full phase diagram, Hixson et al.[17,18] sketched in a bcc-hcp phase line that connected the 210 GPa point to 420 GPa, the pressure at which theoretical calculations predicted Mo, at 0 K, will undergo an bcc-hcp transition as consequence of pressure-induced *s*-*d* electron transfer [19]. If the solid phase above 210 GPa is hcp then, from an inspection of the melting curves in Fig. 1, it is reasonable to expect that on transforming from bcc to hcp the melt curve should stiffen. In order to reconcile the DAC and shock measurements the melting model parameters were adjusted such that the melt curve would stiffen continuously with increasing pressure and converge to the LANL melt point near 370 GPa, the pressure interpreted as the onset of shock melting.

The values of ΔU^{l-s}_{d-band}, which determine the melt slope, are plotted in Fig. 3. From 0 to 100 GPa the values are those from reference [5]. In this pressure range melting is from a bcc structure to a close-packed-like fluid. Above about 210 GPa melting will be from hcp to a close-packed-like liquid. The change in volume and *d*-electron character will be less upon melting from the hcp phase than from bcc. By varying the Friedel parameters continuously with increasing pressure from bcc-liquid to hcp-liquid like melting, ΔU^{l-s}_{d-band} reaches a minimum value near 150 GPa and rises to ΔU^{l-s}_{d-band}=0 near 370 GPa. At this pressure the liquid and solid have the same number of *d*-electrons and cohesive energy, and

the melting temperature is determined solely by the effective ion-ion repulsive potential. Our calculated melting curve which omits the influence of a partially filled *d*-band, labeled $\Delta U^{l-s}_{d-band}=0$, while much stiffer than the DAC measurements, is in reasonable agreement with the shock measurements.

In our revised Mo phase diagram the predicted melting curve remains in good agreement with the DAC measurements up to 90 GPa, the highest pressure at which measurements were made, and is in reasonable agreement with the LANL shock melting point near 370 GPa. But most important is that the stiffening of the melting curve in the hcp phase is consistent with, and a confirmation of the systematic trends observed in Fig. 1.

IV. Fe and Cu.

Because Fe is the dominant component of the earth's core, its melting curve has been a matter of great interest and controversy. Since Fe is a first row transition metal, and also melts from a close-packed structure at high pressure, we expect it to have a melt curve that is similar to Ni, and flatter slope than Cu (Fig.1). Plotted in Fig.4 are the experimental melting curves for Cu[4] and Fe[1], and the *"ab-initio"* theoretical predictions of Vocadlo et al. for Cu[20] and Alfé[21 and Laio[22] for Fe. The DAC experimental melting temperatures of Boehler[1] are significantly lower than those predicted by Alfé but in agreement with Laio. Curiously, although our experimental Cu melting data agrees very well with the theoretical calculations of Vocadlo for Cu, they also agree with the Fe melting calculations of Alfé. The fact that the theoretical melting calculations for Fe and Cu fall on the same P-T curve as the Cu measurements suggests a failure to properly include the role of *d*-band electrons in the Fe calculations. It is likely that this failure stems from the use of spherically symmetric rare-gas-like potentials in a perturbation theory scheme designed to calculate the melt free energy, thereby limiting the behavior of *d*-electrons.

V. Local melt structure

In contrast to the traditional picture of liquid structures based on a dense random packing of hard spheres or rare gas atoms, Frank[23] was the first to suggest that structures of liquid melts could be based on packings of icosahedral clusters consisting of 13 atoms, 12 atoms with fivefold symmetry surrounding a central atom. Frank pointed out that an icosahedral cluster of 13 Lennard-Jones atoms has an energy that is 8.4% lower than a close-packed arrangement. Although it is impossible to create a crystalline structure in which each atom has fivefold symmetry, larger sized randomly packed ISRO clusters may evolve continuously and be interconnected throughout the liquid or glass[24]. Evidence for the presence of ISRO clustering in stable and under-cooled melts of transition metals have been reported by Schenk et al.[25] and Lee et al.[26] using neutron scattering and *in situ* x-ray diffraction methods, respectively. Among these metals are Ni, Fe, Zr[25], Fe, Ti [26]. First principles molecular dynamics simulations made by Jaske et al. [27] found evidence for the existence of short range order in the stable and under-cooled melts of Ni, Zr, and Ta.

The formation of icosahedral clusters in the melt may be thought of in terms of the Jahn-Teller[28] theorem in which a system can be stabilized by a structural distortion that removes the degeneracy of levels, such as in the case of free electrons, by forming bonds. The J-T effect exists in systems in which the highest occupied orbital is degenerate and not fully occupied, such as it is in the case of liquid transition metals with partially filled d-bands, thereby lowering the energy. Since the five-fold symmetry of *d*-electrons energetically favors the formation of an ISRO, it also contributes to a lowering of the melting temperature ($\Delta U^{l\to s}_{d\text{-}band} < 0$).

It is perhaps noteworthy that in the case of Cu, which has a relatively stiff melting curve and a filled *d*-band, that Di Cicco et al.[29] found little evidence from x-ray absorption measurements for icosahedral structure in the liquid but strong evidence for this structure in the Fe melt. The connection between melting, icosahedral structure, *d*-electrons and the Jahn-Teller effect deserves further attention.

VI. Discussion

While the connection between icosahedral clusters, *d*-electrons and melting remains to be clarified, some generalizations may be drawn from the known properties of transition metal clusters [30]. For example, clusters of simple *sp* metals, including Cu, are dominated by the delocalized character of the electrons, while transition metals with an unfilled band reflects the rather localized behavior of *d*-electrons. Consequently, although theoretical predictions of melting curves made using the same effective inter-atomic potential for the solid and liquid have been successful in calculations for Ar, Al and Cu, this has not been generally the case for transition metals. For these three solids the electronic structure remains relatively unchanged upon melting. To summarize, the low melting temperatures and slopes found in transition metals are due to the absence of long range order in the liquid phase which allows for changes in the electron density of states that in turn lower the electron energy. The pressure-induced *s*-*d* transition by increasing the *d*-character allows the lowering to persist to higher pressures thereby maintaining a low melting slope.

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Figure captions.

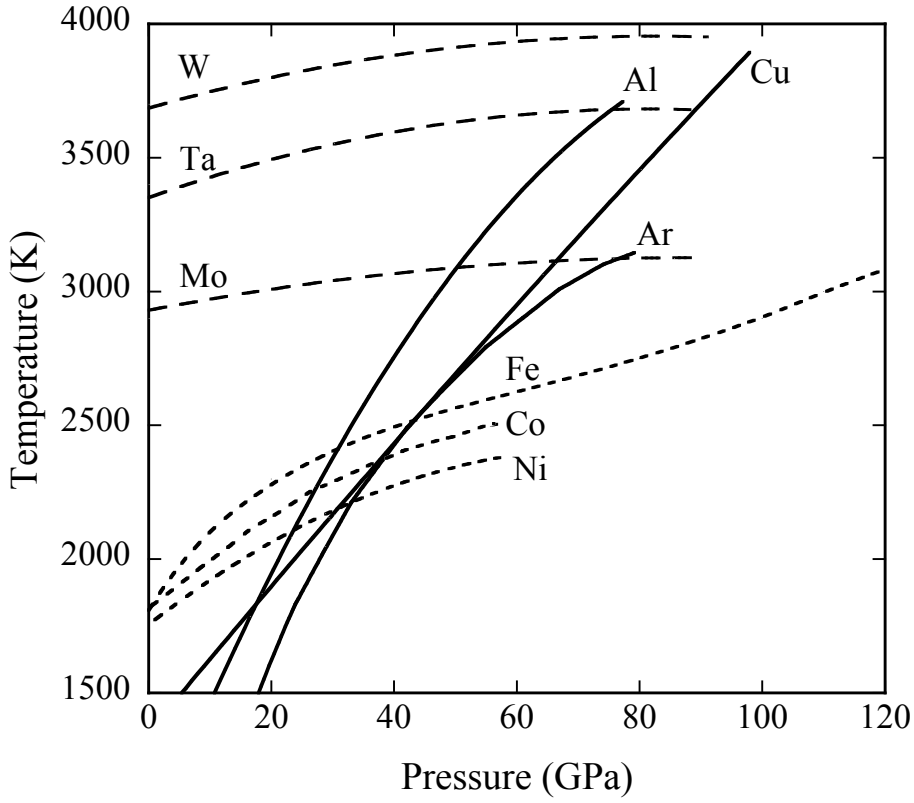
Fig. 1. Melting curves of transition metals. References cited in text.

Fig. 2. Molybdenum phase diagram. DAC melting points to 80 GPa (filled circles)[2]. Theoretical melting curve extended to near 400 GPa (solid curve). Theoretical melting curve which omits the influence of a partially filled d-band and is labeled as $\Delta U^{l\to s}_{d\text{-}band}=0$ (small dashed curve). Calculated Hugoniot[5] (large dashed curve). Large crosses, are for the bcc-hcp shock transition at 210 GPa and the Hugoniot melting point near 370 GPa[6]. A proposed bcc-hcp phase-line[7] (small dashed curve).

Fig. 3. Values of $\Delta U^{l\to s}_{d\text{-}band}$, the change in *d*-band cohesive energy used to calculate the melting curve in Fig. 2.

Fig. 4. Melting curves of Cu and Fe. Experimental DAC melting curves are by Japel[3](filled squares)and Boehler[1], for Cu and Fe respectively. The theoretical melting curves are from Vocadlo [21] for Cu, and from Alfé [22} and Laio[23] for Fe. .

Figure 1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Pressure (GPa)
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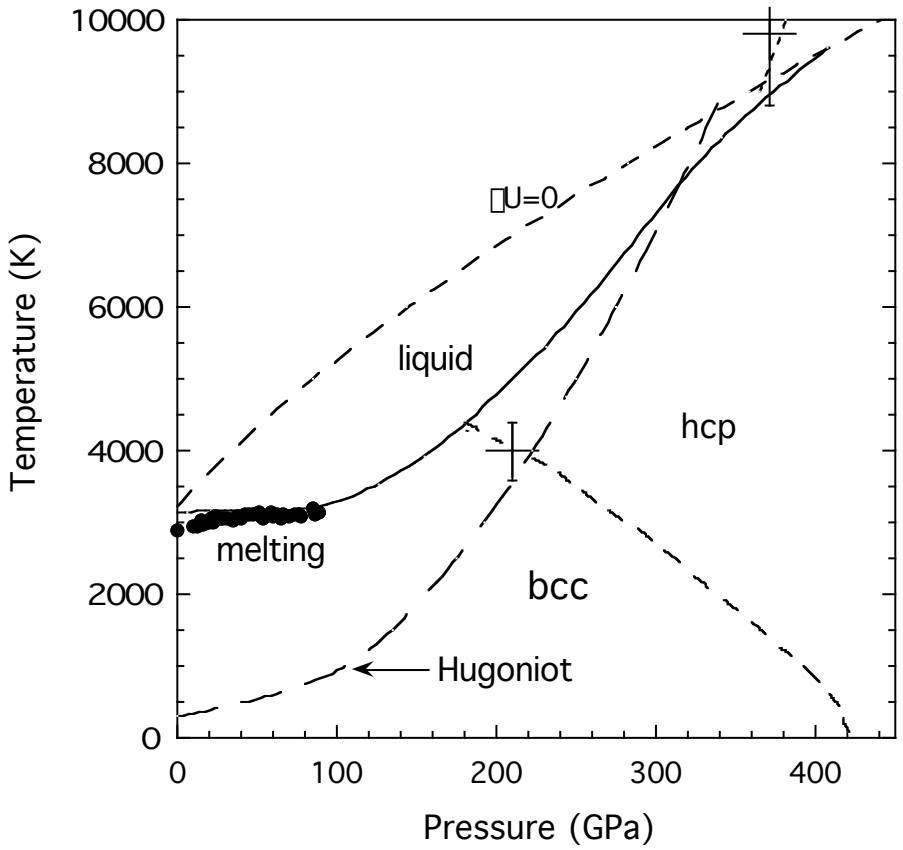
Ta
Mo
Al
Cu
Ar
Fe
Co
Ni

Figure 2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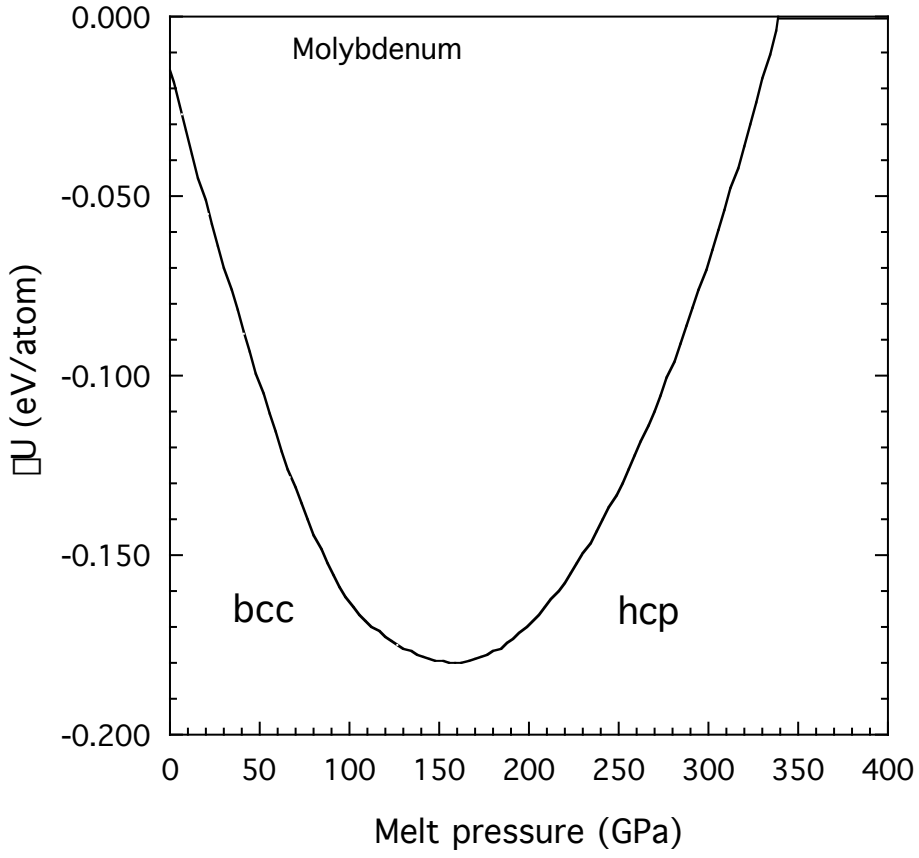
hcp
melting
bcc
Hugoniot

Figure 3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-0.100
-0.150
-0.200
□U (eV/atom)
bcc
hcp
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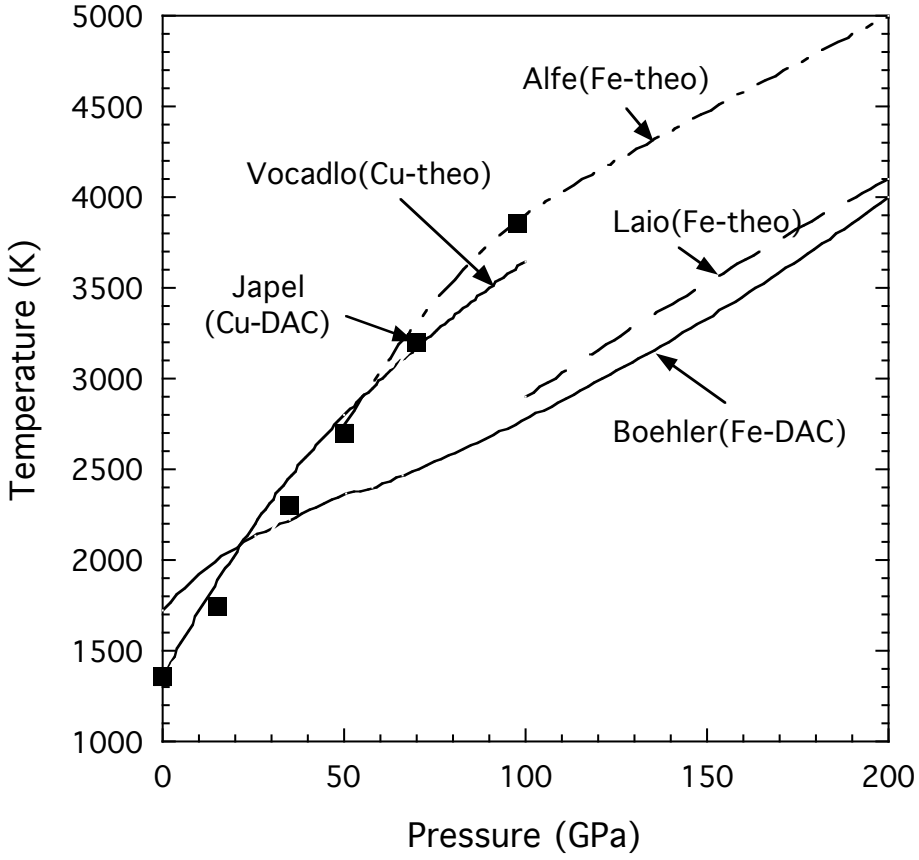
50
100
150
200
250
300
350
400
Melt pressure (GPa)

Figure 4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Vocadlo(Cu-theo)
Laio(Fe-theo)
Japel
(Cu-DAC)
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